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2019

Teinilä , K , Aurela , M , Niemi , J V , Kousa , A , Petäjä , T , Järvi , L , Hillamo , R , Kangas , L , Saarikoski , S & Timonen , H 2019 , ' Concentration variation of gaseous and particulate þÿpollutants in the helsinki city centre observations from a two-year ca þÿ2013 2015 ' , Boreal Environment Research , vol. 24 , pp. 115-136 .

http://hdl.handle.net/10138/312715

publishedVersion

BOREAL ENVIRONMENT RESEARCH 24: 115–136
ISSN 1797-2469 (online)

Helsinki 10 September 2019

Concentration variation of gaseous and particulate pollutants in the Helsinki city centre — observations from a two-year campaign from 2013–2015

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Received 4 Feb. 2019, final version received 4 Jul. 2019, accepted 4 Jul. 2019

Teinilä K., Aurela M., Niemi J., Kousa A., Petäjä T., Järvi L., Hillamo R., Kangas L., Saarikoski S. & Timonen H. 2019: Concentration variation of gaseous and particulate pollutants in the Helsinki city centre — observations from a two-year campaign from 2013–2015. *Boreal Env. Res.* 24: 115–136.

The main chemical composition of PM_1 (total organics, black carbon, sulphate, nitrate and ammonium), mass concentrations of $PM_{2.5}$ and $PM_{2.5–10}$ and concentration of specific trace gases were measured in a high temporal resolution from May 2013 to April 2015 in the city centre of Helsinki, Finland. On average, the concentrations of $PM_{2.5}$ and $PM_{2.5–10}$ were 9.1 μg m^{-3} and 16 μg m^{-3}, respectively, during a two-year campaign. PM_1 consisted mostly of organics (60%), followed by sulphate (12%), black carbon (11%), nitrate (9.8%) and ammonium (6.5%). The particle and gas data were combined with the meteorological data in order to obtain information on how local meteorology affects concentrations of air pollutants. Two meteorological parameters that mostly affected the pollutant concentrations were the wind speed and temperature, while sulphate and $PM_{2.5–10}$ were also impacted by the relative humidity. The highest concentrations of the measured PM_1 components were observed when the wind was calm or the temperature was either very cold or very warm. $PM_{2.5–10}$ concentrations were at the highest during calm or very windy conditions, due to local street and construction dust. The seasonal- and diurnal-varying mixing height did not seem to affect markedly the concentrations of pollutants. Overall, air quality in terms of the aerosol mass was governed by three different main pollution sources in the Helsinki city centre: 1) local sources, of which traffic-related emissions were the most important; 2) long-range or regional transport of pollutants; and 3) local sources of organic aerosol.

Editor in charge of this article: Veli-Matti Kerminen

Introduction

The long-term exposure of elevated concentration of air pollutants, such as particulate matter (PM) and gaseous compounds like nitrogen oxides (NO, NO_2) and ozone (O_3), can have adverse effects on human health (Atkinson *et al*. 2014). At the global level, the exposure to outdoor air pollution, mostly to PM, causes 3.3 million premature deaths/year and it is estimated that by 2050, the contribution of outdoor air pollution to premature mortality could be doubled (Lelieveld *et al*. 2015). The relative contributions of different air pollution sources may vary significantly, but e.g., in densely-populated western countries, 33–55% of premature deaths are related to traffic and power generation (Lelieveld *et al*. 2015). Especially fine particles (< 1 μm or 2.5 μm in diameter) are considered harmful as they can be transported deep into the human respiratory tract (Zanobetti *et al*. 2014).

Helsinki is the largest city in Finland with ~650 000 inhabitants. Compared to many other cities around the word, the air quality in Helsinki is relatively good for most of the time, however, PM and NO_2 concentrations can occasionally be elevated. It has been shown in earlier studies that the main local anthropogenic fine particle sources in Helsinki metropolitan area are direct vehicular emissions and residential wood burning (Aurela *et al*. 2015, Carbone *et al*. 2013, Saarikoski *et al*. 2008, Järvi *et al*. 2008, Pirjola *et al*. 2017). Other anthropogenic sources affecting PM concentrations are e.g., road dust, energy production and ship emissions (Kupiainen *et al*. 2016, Soares *et al*. 2014). From time to time, Helsinki is also affected by pollution episodes, during which elevated concentrations of $PM_{2.5}$ are measured. These $PM_{2.5}$ episodes are typically due to: 1) strong long-range transportation (LRT) from Europe; 2) regional or long-range transported smoke from forest fires; or 3) wintertime inversion when locally-produced pollutants are trapped in the planetary boundary layer over the city (Leino *et al*. 2014, Niemi *et al*. 2004, 2005, 2009, Pirjola *et al*. 2017).

In order to improve urban air quality, detailed information on the chemical composition, concentrations, sources and removal mechanism of particles and gases (e.g., NO, NO_2) and oxidants (e.g., O_3) are needed. The majority of ground level NO_x (= NO + NO_2) originates from traffic sources in urban areas (Karppinen *et al*. 2000, Lähde *et al*. 2014), whereas O_3 is formed in the lower troposphere via photochemical reactions between nitrogen oxides and volatile organic compounds (VOC) emitted from motor vehicles, biomass burning and vegetation (e.g. Rönkkö *et al*. 2013, Pirjola *et al*. 2015, Tröstl *et al*. 2016). In Helsinki, a large amount of O_3 is long-range or regionally transported (Laurila *et al*. 1996). Dry and wet deposition as well as chemical reactions are important mechanisms that remove gaseous and particulate pollutants from the atmosphere or reduce their concentrations.

In this study, we show the general overview of the chemical composition and concentrations of particles and gases over a two-year period in the city centre of Helsinki, Finland. The long-lasting measurement campaign with a high-time resolution of the chemical composition enables us to investigate the seasonal variation of many components, which has not been previously studied of Helsinki — as previous campaign durations have typically lasted from a few weeks to months. Finally, a very important objective is to study how meteorological parameters affect the local air quality.

Materials and methods

Measurement site

Particle and gas measurements were carried out for two years (May 2013–April 2015) at the air quality monitoring station of HSY (Helsinki Region Environmental Services Authority) in Helsinki, Finland (60°17′N, 24°93′E). The measurement site was located at a curbside of a thoroughfare (Mannerheimintie 5) with the traffic flow of 19 000 vehicles/working day (approx. 7% of heavy-duty vehicles). Mannerheimintie is 47-m wide with four driving lanes and tram rails located in the middle of the street. Between the measurement station and the driving lanes, there is a 1.5-m-wide cycling lane. The distance to the nearest street intersection is 35 m. The speed limit at the area is 30 km h^{-1}. In general, the measurement station is considered to repre-

sent the air quality in a busy area of the Helsinki city centre, with a high contribution of vehicular traffic emissions and pedestrian traffic. Both sides of the street have a constant row of buildings (six blocks), which affect the dispersion of emissions, so the site has the characteristics of a street canyon (Pirjola *et al*. 2012). This has to be kept in mind when interpreting the measurement results. The distance from the station to the nearest building (37 m height) is six metres. Samples for the instruments were taken four metres above the ground level.

PM, trace gas and meteorology measurements

The chemical composition of PM_1 was measured continuously using an Aerosol Chemical Speciation Monitor (ACSM; Aerodyne Research Inc.; Ng *et al*. 2011). The ACSM characterises non-refractory aerosol species (total organics, sulphate, nitrate, ammonium and chloride) with a time resolution of approximately 30 minutes. The ACSM is able to measure submicron particles that pass through the aerodynamic lens (50% transmission range of the lens is 75–650 nm, Liu *et al*. 2007). The flow into the ACSM, controlled by a critical orifice, was roughly 0.1 lpm (liters per minute), but a by-pass flow of 3 lpm was used to get particles efficiently close to the inlet of the ACSM. A cyclone (URG, URG-2000-30ED) was installed before the ACSM inlet to remove particles larger than 2.5 μm (aerodynamic diameter) to preventing clogging the critical orifice. The sensitivity of the ACSM is 0.3, 0.04, 0.02, 0.5 and 0.02 μg m^{-3} for organics, sulphate, nitrate, ammonium and chloride, respectively, for the 30-minute time resolution as reported by the manufacturer. The accuracy of the ACSM measurements is around 30% (Crenn *et al*. 2015, Budisulistiorini *et al*. 2014).

The collection efficiency (CE) that takes into account particle losses in the vaporizer of the ACSM (Canagaratna *et al*. 2007) was calculated according to Middlebrook *et al*. (2012). The relative humidity of the sample flow varied between 20% and 50% (May 2013–April 2015) and hence, was not taken into account in the CE calculation (Middlebrook *et al*. 2012). The concentration of ammonium nitrate was very low in the Helsinki city centre, so it has no effect on the collection efficiency. The measured aerosol was highly neutralized and the calculated CE values were below 0.5 when the concentration of ammonium was above the detection limit. Hence the collection efficiency of 0.5 was used throughout the ACSM measurements when calculating the concentrations. The ACSM was calibrated for the response factor (RF) of nitrate and for the relative ionization efficiency (RIE) of ammonium and sulphate by atomising ammonium nitrate and diammonium sulphate solution with a known particle diameter (300 nm). Calibrations were done using the jump scan mode, in which only specific ions of nitrate (NO^+ and NO_2^+), ammonium ($NH^+$and $NH2^+$) and sulphate (SO^+, SO_2^+, SO_3^+ and SO_4^+) were monitored. Due to technical problems, ACSM data were not available from December 2014 to January 2015.

Black carbon (BC) concentration was measured using a multi-angle absorption photometer (MAAP; Model 5012; Thermo Electron Corporation; Petzold and Schönlinner 2004). The MAAP determines the absorption coefficient (σ_{AP}) of the particles deposited on a filter by a simultaneous measurement of transmitted and backscattered light. The value of σ_{AP} is converted to a BC mass concentration by the instrument firmware using a mass absorption cross section of 6.6 m^2 g^{-1} (Petzold and Schönlinner 2004). The detection limit of the MAAP, as reported by the manufacturer, is 0.05 μg m^{-3}, and the measurement range is from 0–180 μg m^{-3} when a ten minutes averaging time is used. The MAAP measured with a one-minute time resolution. A cyclone/PM_1 inlet was used to cut off particles above 1 μm.

Mass concentrations of $PM_{2.5}$ and PM_{10} particles were measured based on the β-attenuation using two instruments (FH 62 I-R; Thermo Electron Corporation). The detection limit of the FH 62 I-R, as reported by the manufacturer, is 0.5 μg m^{-3}, and the measurement range is from 0–5000 μg m^{-3} when a ten-minute averaging time is used. Data were obtained with a one-minute time resolution. The mass concentration of coarse particles ($PM_{2.5–10}$) was calculated by subtracting the $PM_{2.5}$ mass concentration from the PM_{10} mass concentration. In this paper, the term submicron particles (< 1.0 μm) is used when the discus-

sion concerns PM_1 particle chemical composition measured with the ACSM and MAAP, while the term, fine particles (< 2.5 μm) is used for $PM_{2.5}$ mass concentrations measured with the Thermo FH 62 I-R instrument. Gas concentrations were continuously measured with a one-minute time resolution (O_3, NO, NO_2). The concentration of NO_x (in mass concentration) was calculated using the formula $NO_x = NO + 1.53 \times NO_2$.

Meteorological data, except total radiation, were obtained from the Finnish Meteorological Institute (FMI) monitoring station in Helsinki, Kaisaniemi, located less than one kilometre from the measurement site (measurement height 27 m). Total radiation data were obtained from the Finnish Meteorological Institute (FMI) Kumpula station about five kilometres northeast from the measurement site. The measurement devices used to measure the concentration of gaseous compounds and meteorological parameters are listed in Table 1. The mixing height was calculated using the model developed at FMI (MPP-FMI; Karppinen *et al*. 2001). All the particle and gas data were averaged for hourly results. Back trajectories of air masses arriving at the measurement site were calculated using the NOOA HYSPLIT model (Stein *et al*. 2015, Rolph *et al*. 2017). The 96-hour back trajectories were calculated for every one hour for 100 m a.s.l. The data analysis was made using the R software (R Core Team 2019) and R package *openair* (Carslaw and Ropkins 2012).

The measured chemical components in PM_1 (the sum of organics, sulphate, nitrate, ammonium, chloride, and BC) explained, on average, 80% of the measured fine particle mass ($PM_{2.5}$) and the correlation between the sum of chemical components and $PM_{2.5}$ was high ($r^2 = 0.82$ for daily concentrations, Pearson correlation; Appendix Fig. A1). The different cut-off sizes used for the measurements of the particle chemical composition (PM_1: ACSM, MAAP) and mass ($PM_{2.5}$: β-attenuation) explain partly this observed difference. In addition, the ACSM does not measure components like road dust, sodium chloride (originating from sea salt particles and used also to prevent road slipperiness). The majority of these components are found in the particles larger than 2.5 μm, but to some degree, these components can also be found in $PM_{2.5}$.

Results and discussion

General features of fine particulate and gaseous pollutants in the city centre in 2013–2015

The average mass concentration of $PM_{2.5}$ was 9.1 μg m^{-3} during the two-year campaign in the

Table 1. Measurement devices used for monitoring concentration of gaseous compounds and meteorological parameters. MR, DL and TR indicate the measurement range, detection limit and time resolution of the device, respectively.

Monitoring devices for gaseous components and meteorological parameters		
Gaseous compounds	Model	MR, DL, TR
NO and NO_2 (Mannerheimintie & Luukki)	APNA-370, Horiba	0–1 ppm, 0.5 ppb, 1 min
O_3 (Mannerheimintie)	APOA-370, Horiba	0–1 ppm, 0.5 ppb, 1 min
O_3 (Luukki)	Thermo Electron Model 49i	0–1 ppm, 0.5 ppb, 1 min
Meteorological parameters		
Gaseous compounds	Model	
Relative humidity	HMP35 ja HMP45D, Vaisala Oyj	
Pressure	PTB201A ja PTB220, Vaisala Oyj	
Wind speed and direction	UA2D, ultrasonic anemometer, AdolfThies GMBH & Co. KG	
Global radiation	CM11, thermopile pyranometer, Kipp & Zonen B. V.	

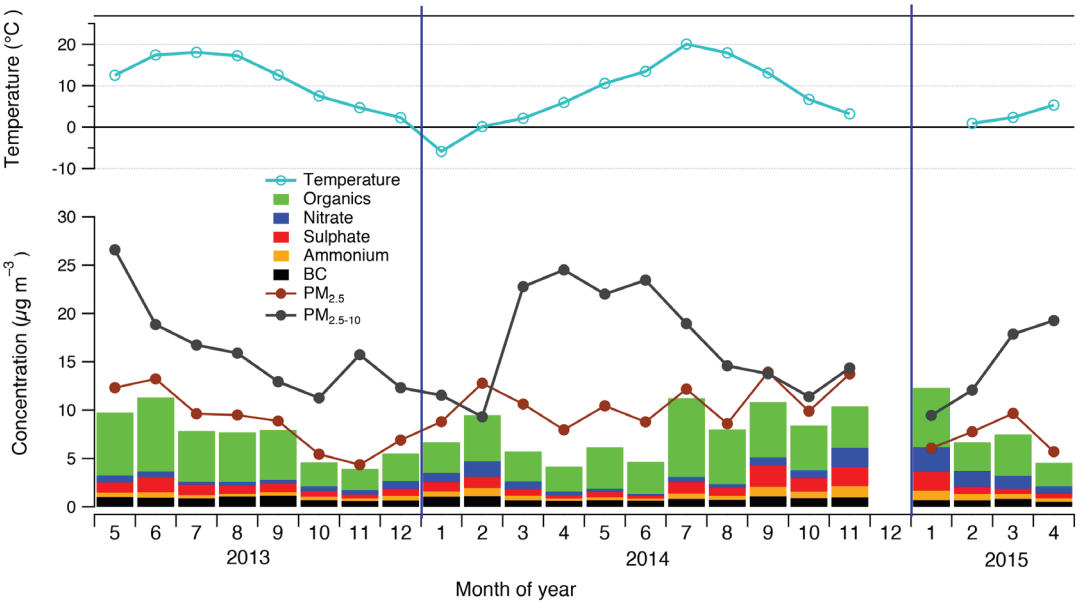

Fig. 1. Monthly-averaged mass concentrations of $PM_{2.5}$, $PM_{2.5–10}$ and measured chemical components of submicron particles in the Helsinki city centre from May 2013 to April 2015. Monthly-averaged temperatures are shown in the upper subfigure. Organics, nitrate, sulphate and ammonium were measured with the ACSM, BC with the MAAP, and $PM_{2.5}$ and $PM_{2.5–10}$ with the β-attenuation method.

Helsinki city centre. The composition of submicron particles was dominated by organics with an average contribution of 60% to the analysed mass (Fig. 1). The hourly mass concentration of organics varied between 0.05–34 μg m^{-3} (2-year average: 4.4 μg m^{-3}). The relative abundances of the other measured chemical components were 12% (average: 0.9 μg m^{-3}), 11% (average: 0.8 μg m^{-3}), 9.8% (average: 0.7 μg m^{-3}) and 6.5% (average: 0.5 μg m^{-3}) for sulphate, black carbon, nitrate and ammonium, respectively. The average concentration of chloride was only 0.02 μg m^{-3} during the measurement period and therefore chloride was not included in the following discussion. The hourly-averaged concentration of NO_x was 76 μg m^{-3} (22 μg m^{-3} for NO and 32 μg m^{-3} for NO_2) and the hourly-averaged concentration of O_3 was 37 μg m^{-3} during the campaign.

Mass concentration of coarse particles

On average, the $PM_{2.5–10}$ concentration at the site was 16 μg m^{-3}. During spring 2014 there was an intensive road dust episode causing elevated $PM_{2.5–10}$ levels when monthly $PM_{2.5–10}$ concentrations were roughly 80–100% higher than the average $PM_{2.5–10}$ concentration. Road dust episodes are typical in Finland during spring when mineral dust from asphalt wear and sanding materials as well as de-icing salts are accumulated in icy, snowy and moist street environments in winter and released into the air in spring as the street surfaces dries out (Kupiainen *et al*. 2016). Additionally, during the summer of 2014, construction work (buildings and streets) took place near the measurement site, which was seen as elevated mass concentrations of coarse particles. Most probably also fine particles contained particulate matter from these same sources, including mineral dust which cannot be detected with the ACSM, thus increasing the difference between the sum of the measured chemical components and $PM_{2.5}$ between March and July 2014 (Fig. 1). The ratio of measured PM_{10} and $PM_{2.5}$ from March–June 2014 was larger than 4, whereas the average ratio was 2.5. The observed $PM_{2.5}$ and $PM_{2.5–10}$ concentrations were similar to those reported by Malkki *et al*. (2018),

who also showed a decreasing trend of $PM_{2.5}$ and $PM_{2.5–10}$ in the Helsinki city centre since the start of their measurements in 2005.

Temporal variations of pollutants

In general, when the morning rush hour started, the concentration of NO_x rose while that of O_3 decreased. After noon, the O_3 concentration returned to its pre-morning level, which was probably because 1) O_3 was transported to the ground level from the upper troposphere when the mixing height was at its maximum and 2) the concentration of NO_x decreased after the morning rush hour was over. The O_3 depletion, likely caused by high NO_x emissions from vehicles ($NO + O_3 \rightarrow NO_2$) during the morning rush hour, was not seen in the HSY air quality monitoring station situated at the Luukki rural site in the Helsinki Metropolitan area (64°53´N, 25°50´E, ~22 kilometres northwest from the Helsinki city centre; Appendix Fig. A2), nor during the weekends at the city centre site (Fig. 2). This is expected because the average NO_x concentration at the rural remote site was only 8.5 μg m^{-3}, whereas in the city centre it was 76 μg m^{-3}. In addition, the average NO concentrations were 0.35 μg m^{-3} and 21.9 μg m^{-3} in rural remote and the city centre sites, respectively. The low amount of NO at the remote site restricts the O_3 depletion. In addition to this, the O_3 concentration at the remote site also showed a much clearer diurnal cycle (Appendix Fig. A2), which was caused either by the transportation of O_3 to the ground level or production of O_3 via photolytic reaction of NO_2 in the afternoon due to increased solar radiation, especially in spring and summer. According to this, it seems that in the Helsinki city centre, mainly long-range transported O_3 is destroyed effectively by the locally-emitted pollutant NO_x, with a high fraction of NO, during daytime when the traffic frequencies are high (Anttila *et al*. 2011). The average O_3 concentration during the measurements was also lower at the city centre site (37 μg m^{-3}) than at the background site of the Helsinki Metropolitan area (51 μg m^{-3}). However, in spring and summer, a slight increase in the O_3 concentration was seen in the afternoon also in the Helsinki city centre. It is possible that in the afternoon, O_3 was also formed in the Helsinki city centre via a photolytic reaction of NO_2.

Similarly to NO_x, the concentrations of BC and $PM_{2.5–10}$ showed a rapid increase during the morning hours (starting from 06:00), which is expected as they originate directly or indirectly from the nearby traffic. BC is a primary pollutant emitted directly from the motor vehicle engines and also NO_x is related to primary engine emissions, whereas $PM_{2.5–10}$ consists mostly of re-entrained road dust, the concentration of which increases during the morning rush hour as vehicles pass the site. As already mentioned, $PM_{2.5–10}$ concentrations were the highest during spring due to road dust episodes, while elevated concentrations of $PM_{2.5–10}$ were also observed in early summer due to dust from the construction works (Appendix Fig. A3). Enhanced concentrations of $PM_{2.5–10}$ were also measured in November. One explanation for this could be that many vehicles are equipped with studded tires in November, which can release dust from the road. However, when looking at the hourly measurement data, it revealed that the elevated $PM_{2.5–10}$ concentrations were related to temperatures near or below 0 °C, so it is possible that sanding of pavements had already started during cold days, or that the streets got dry at lower temperatures. $PM_{2.5}$ did not have any clear diurnal (Fig. 2) or seasonal trends (not shown). The lack of clear diurnal cycle for $PM_{2.5}$ was due to the fact that it consisted of aerosol from two different local sources, with traffic-related particles dominating during the morning hours and other sources, containing mostly organics, starting to dominate in the afternoon (discussed later).

In the atmosphere, particulate matter is also formed via the oxidation of gaseous compounds like NO_x, SO_2, and VOCs (Timonen *et al*. 2017, Karjalainen *et al*. 2016, Pirjola *et al*. 2015), followed by condensation of the oxidation products (sulphate, nitrate and oxidized organic matter) onto pre-existing particles or in some cases by new particle formation (Nieminen *et al*. 2018, Kulmala *et al*. 2003,

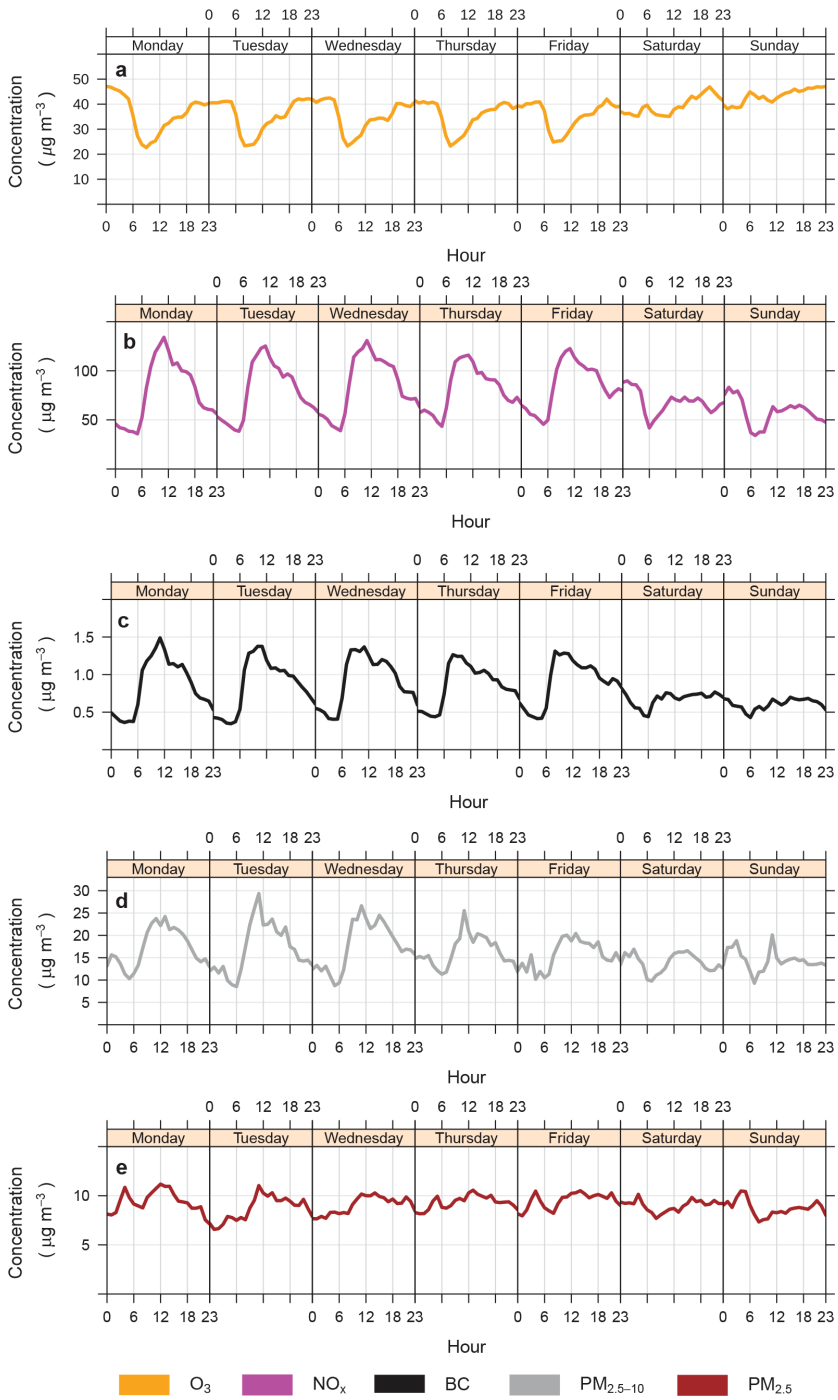

Fig. 2. Daily diurnal variations of (**a**) O_3, (**b**) NO_x, (**c**) BC, (**d**) $PM_{2.5–10}$ and (**e**) $PM_{2.5}$. Notice the different y-scale limits for each parameter.

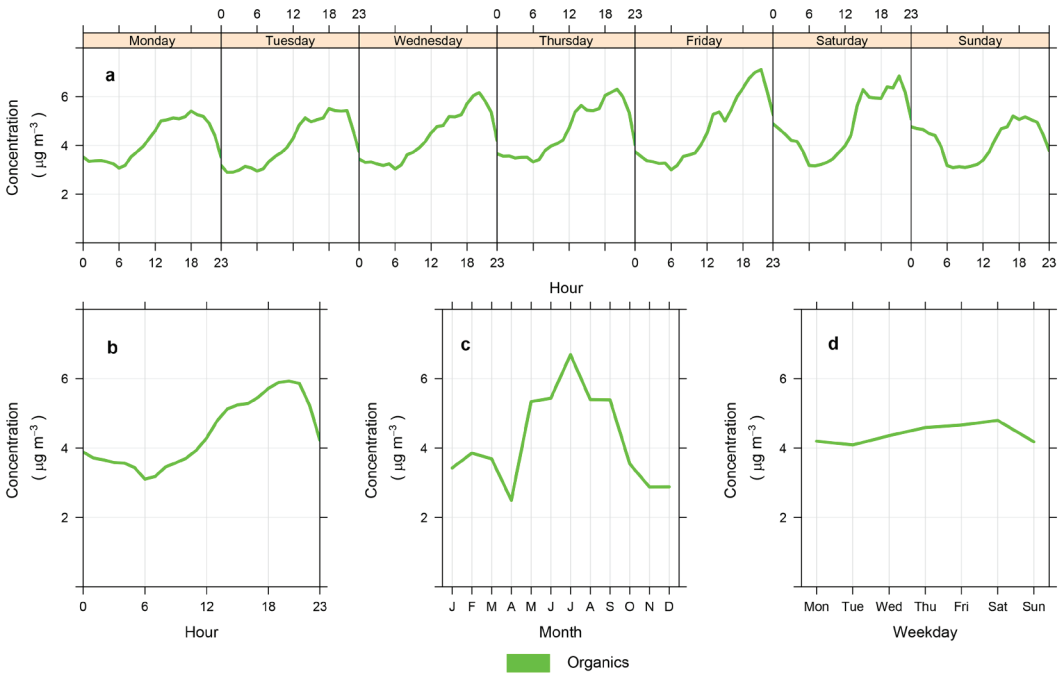

Fig. 3. The (**a**) weekly, (**b**) hourly, (**c**) monthly and (**d**) daily variations of total organics in PM_1 in the Helsinki city centre between May 2013 and April 2015.

Boy *et al*. 2005). Sulphate and nitrate are typically found in aged aerosol particles together with ammonia, which neutralizes the acidic aerosol. The measured PM_1 in the Helsinki city centre was also neutralized by ammonia (Appendix Fig. A4). None of these inorganic compounds showed a very clear diurnal pattern (Appendix Fig. A5). The lack of a diurnal pattern and the high neutralization of inorganic ions indicate that the aerosol sulphate and nitrate together with ammonium were long-range transported to the measurement site. Sulphate showed slightly elevated concentrations during the afternoon hours, which may be connected to a more effective transport of long range-transported sulphate aerosol from the upper troposphere to the ground level. Nitrate, on the other hand, showed lower concentrations during the afternoon, which is due to evaporation of nitrate at elevated temperatures, especially during the warmer season. A similar temporal effect was seen as slightly higher nitrate concentrations during the winter. Sulphate or ammonium had no clear temporal trend.

The concentration of particulate organics showed a clear seasonal cycle with the highest concentrations during the warmest months (Fig. 3). A similar seasonal cycle for organics in Helsinki was also reported by Timonen *et al*. (2014). The diurnal cycle of organics differed clearly from those of primary traffic-related pollutants (BC, NO_x). The concentration of organics showed maximum values during the afternoon and evening (Fig. 3), and the enhanced afternoon and evening concentrations were seen in all days, although the maximum concentration was slightly lower on Sundays. The source of this organic aerosol in the Helsinki city centre is not quite clear but its strong diurnal variation indicates a local source.

One possible source of primary organic aerosol, other than traffic, could be local or regional biomass burning. The residential heating with wood was shown to be a notable source of organics in the Helsinki metropolitan area in wintertime, but not in the city centre (Aurela *et al*. 2015, Pirjola *et al*. 2017, Saarnio *et al*. 2012). Based on the similar diurnal patterns in different seasons and lower concentra-

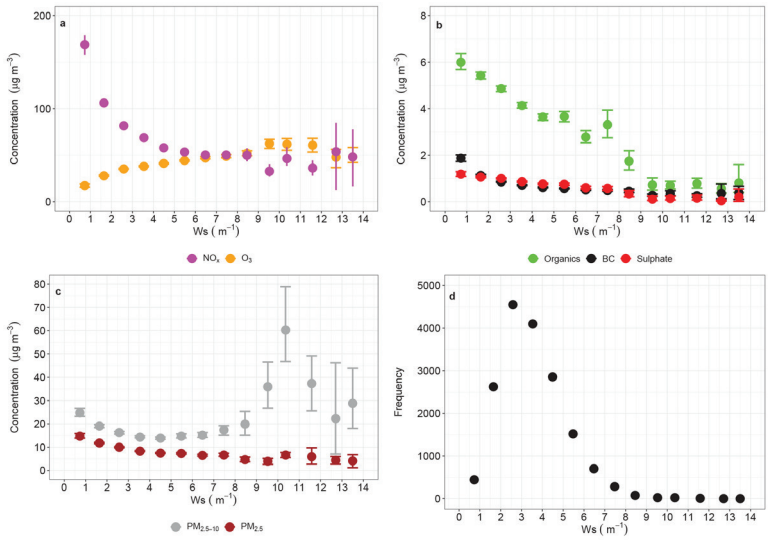

Fig. 4. Concentration of (**a**) NO_x and O_3, (**b**) organics, BC and sulphate and (**c**) $PM_{2.5–10}$ and $PM_{2.5}$; in panel (**d**), the measured wind speed frequencies as a function of wind speed in the Helsinki city centre between May 2013 and April 2015.

tions of organics in winter, suggest that local biomass burning emission did not have a substantial effect on the concentration of organics in the Helsinki city centre. In summertime, such a source is not relevant. Although there are studies showing that cooking operations contribute significantly to an urban organic aerosol (OA), e.g., in Barcelona (Mohr *et al*. 2012) and in Paris (Crippa *et al*. 2013), earlier measurements in the Helsinki city area showed that the contribution of a cooking factor is not important in the Helsinki city area (Aurela *et al*. 2015, Carbone *et al*. 2014, Crippa *et al*. 2014). Another possible source of organics is locally-produced secondary organic aerosol (SOA) from organic precursor gases. The similar diurnal patterns and concentrations during Saturday and weekdays indicate that these precursor gases were not directly connected to traffic-related emissions. However, some indirect evidence on SOA formation was seen during summer, as organics had the highest concentrations during the warmest months. The major part of SOA is formed in the atmosphere via oxidation of VOCs by OH radicals and O_3. In summer, in addition to higher incoming solar radiation (Appendix Fig. A6), absolute water content (Appendix Fig. A7) and O_3 (Appendix Fig. A2) concentrations were higher. Gas-to-particle conversion contributes both to the increase in aerosol number via secondary processes and secondary aerosol mass (Ehn *et al*. 2014). The lower organic concentration in April may be connected to a low abundance of water vapour in the air (Appendix Fig. A7).

Effect of meteorology on pollutant concentrations

Measured meteorological parameters (wind speed, temperature, radiation and relative humidity) and modelled mixing height showed clear seasonal and diurnal patterns (Appendix Fig. A6). Since Helsinki is situated at a high latitude, the seasonal variation in radiation is large, which has a direct effect on the temperature, mixing height and relative humidity. The greatest diurnal variations in the meteorological parameters were typically seen during the summer months, except for the wind speed which had the largest variations in spring. Based on the two-year measurements, we characterised the influence of local meteorology on the pollutant concentrations in the Helsinki city centre. Hourly pollutant concentrations during the whole measurement campaign were averaged for the wind speed, temperature, relative humidity and mixing height bins in order to reveal their possible correlations. In addition, the effect of wind direction to the highest measured local pollutant concentrations (75th

percentile) was analysed and the effect of meteorology was studied using a simple multilinear regression analysis.

Wind speed and wind direction

The concentration of $PM_{2.5}$ and its individual components (BC, organics and sulphate) decreased with an increasing wind speed (Fig. 4). A similar decrease was also found for ammonium and nitrate (not shown). For the gaseous pollutants, the concentration of NO_x showed a similar decreasing trend with an increasing wind speed. It seems that with low wind speeds, the pollutants were not effectively removed from the measurement site located at the street level and the concentrations of traffic-related pollutants (BC and NO_x) as well as $PM_{2.5}$ (and its component) were elevated. Earlier studies found similar dependencies between the pollutant concentrations and winds speed (e.g., Jones *et al*. 2010, Gasmi *et al*. 2017, Zhang *et al*. 2015, Prosmitis *et al*. 2003). For most of the $PM_{2.5}$ components (organics, sulphate, nitrate and ammonium), the decrease of their concentration as a function of wind speed was nearly linear. However, the concentration of traffic-related pollutants (BC and NO_x) appeared to decrease more rapidly, following an exponential decrease. $PM_{2.5–10}$, on the other hand, showed slightly elevated concentrations with low wind speeds (< 3 m s^{-1}) but quite similar concentrations when the wind speed was between 3 m s^{-1} and 6 m s^{-1}. When the wind speed exceeded 6 m s^{-1}, the concentrations of $PM_{2.5–10}$ started to rise (Fig. 4). High wind speeds may blow soil particles and road dust more effectively into the surrounding air. A similar U-shaped curve between $PM_{2.5–10}$ and wind speed observed by Harrison *et al*. (2001) was explained with two processes affecting the concentration of $PM_{2.5–10}$. Below a certain wind speed threshold, an increasing wind speed dilutes $PM_{2.5–10}$ concentrations but above this limit $PM_{2.5–10}$ concentrations increase with an increasing wind speed due to a suspension of coarse particles. However, it has to be kept in mind that on average, higher wind speeds are measured in the spring (Appendix Fig. A6) when the road dust episodes occur. Also the number of the measurement points with the highest wind speed is limited, which may overestimate the effect of the highest wind speeds.

The O_3 concentration showed a clear increasing trend with an increasing wind speed (Fig. 4). The likely explanation for this is that with higher wind speeds, nitrogen oxides that destroy ozone were removed more effectively from the surrounding air. Wind also transports air masses to the measurement site from locations outside the city centre. This air is probably not as polluted and has a higher O_3 content.

The influence of wind direction on the local pollutant concentrations (BC, NO_x, $PM_{2.5–10}$ and organics) is more complicated because the measurement site has the characteristics of a street canyon. The meteorological data were obtained from the FMI Kaisaniemi measurement station where the measurement height was 27 m. Both wind direction and wind speed may vary markedly at the Mannerheimintie site from that measured at Kaisaniemi.

In order to get information on how the wind direction and wind speed together affect local pollutant concentrations in the Helsinki city centre, bivariate polar plots of local pollutants as a function of wind direction and wind speed were made. Since the interest was on pollution episodes, bivariate polar plots contain only the situations when the highest concentrations (75th percentile) of the pollutants were measured. The conditional probability function (CPF; Ashbaugh *et al*. 1985, Uria-Tellaetxe and Carslaw 2014) was used as a statistical method when calculating the concentrations for each wind speed and direction bins. The concentrations corresponding to the 75th percentiles were above 1.1 μg m^{-3} for BC, 100 μg m^{-3} for NO_x, 21 μg m^{-3} for $PM_{2.5–10}$ and 6.1 μg m^{-3} for organics.

The probabilities that the concentration of the pollutants related to motor engine emissions (BC and NO_x) showed typically high values at low wind speeds (Appendix Fig. A8). The sectors pointing north-west and south-east relate to the orientation of Mannerheimintie and may be related to both higher emissions and more freely-moving air masses over an open street. The sector north-west to north-east, which also

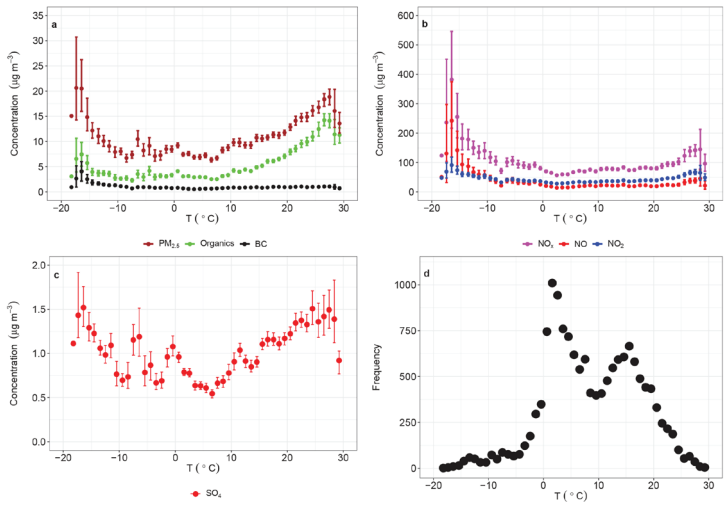

Fig. 5. Concentration of (**a**) BC, organics, $PM_{2.5}$, (**b**) NO_x together with NO and NO_2 and (**c**) sulphate; in panel (**d**), the measured temperature frequencies for different bins as a function of temperature.

showed higher probabilities for high concentrations of BC and NO_x, is heading towards the nearest high building. It is possible that the actual source for high pollutant concentrations is the driving lane from where the pollutants are transported to the measurement site due to vortex formed inside a street canyon (Vardoulaksi *et al*. 2003, Ashbaugh *et al*. 1967). It has also been shown by numerical simulations (Zhang *et al*. 2015) that with an increasing angle between the wind direction and street canyon, the accumulation of pollutants on the ground level is increased. It is not quite clear why the concentration of BC and NO_x showed high probabilities for high concentrations with high northerly wind speeds.

The probabilities of measuring high concentrations of $PM_{2.5–10}$ showed the highest values with high wind speeds. During spring when the Helsinki city centre is typically affected by road dust episodes, the high probabilities spread over a wide range of wind sectors. However, it seems that one source area of $PM_{2.5–10}$ is the sector between west and north, where an intersection with high traffic frequencies is situated. During summer, the sector towards south-east also showed high probabilities for enhanced $PM_{2.5–10}$ concentrations. This same sector also dominated the high probabilities of finding high organic concentrations, except in winter. It is possible that this sector is related to some local source of organic aerosol. However, it has to be pointed out again that this analysis may suffer from uncertainties related to the use of measured wind direction outside the street canyon.

Temperature

The concentration of main pollutants (BC, organics, $PM_{2.5}$ and NO_x together with NO and NO_2) as well as the concentration of sulphate as a function of temperature are shown in Fig. 5. The concentration of $PM_{2.5}$ increased with an increasing temperature. This is expected because the concentration of organics is higher in the summertime and organics are the dominant fraction in $PM_{2.5}$. The increase in $PM_{2.5}$ together with particulate organics is likely due to more effective photochemical reactions producing SOA during the summertime. The increase in the sulphate concentration with an increasing temperature might also be explained by more favourable conditions of sulphate production during the summer (high solar radiation and air water content). The concentration of NO_x increased with an increasing temperature as well, even though to a lesser extent than organics or sulphate.

The concentration of $PM_{2.5}$, NO_x, organics, BC and sulphate showed also elevated concentrations in temperatures below –5 °C. The two points corresponding to temperatures below –17 °C showed lower concentrations, but this may be due to the fact that these points con-

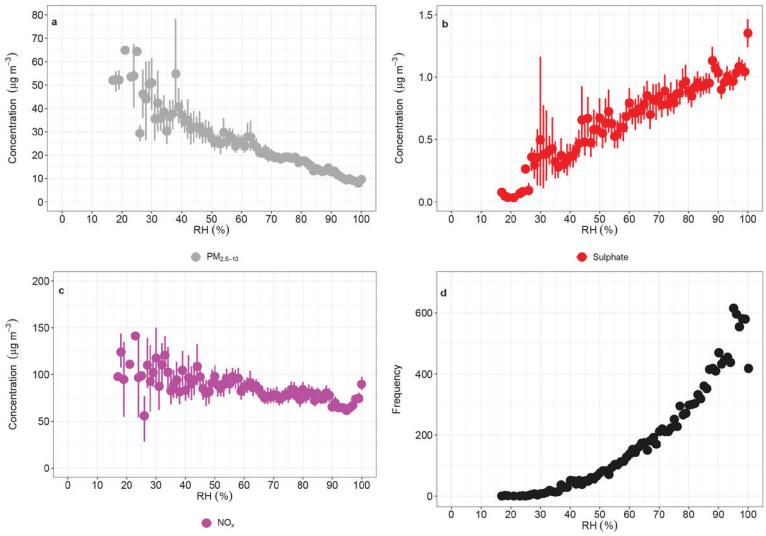

Fig. 6. Concentration of (**a**) $PM_{2.5–10}$, (**b**) sulphate and (**c**) NO_x; in panel (**d**), the measured RH frequencies as a function of relative humidity between May 2013 and April 2015 in the Helsinki city centre.

tain only one to four (consecutive) measurement points. During the period corresponding to these points, calculated back trajectories showed that clean arctic air masses were arriving at the site. Although on average, higher wind speeds are measured during winter, the lowest winds speeds measured during the two-year period were related to the situations with temperatures below –10 °C and with the lowest mixing heights, so the elevated pollutant concentrations were connected with cold temperatures and low wind speeds with a very low mixing height. Additionally, a cold start in vehicles increases NO_x and particle emissions, and also exhaust after treatment systems may not work at low temperatures (Matthaios *et al*. 2019). If looking separately the dependence of NO and NO_2 on temperature, it was found that NO showed higher concentrations at low temperatures compared to NO_2 and vice versa at high temperatures (Fig. 5 and Appendix Fig. A9).

Relative humidity

The concentration of sulphate and coarse particles ($PM_{2.5–10}$) showed a clear correlation with the ambient relative humidity. The sulphate concentration increased with an increasing relative humidity (Fig. 6), which is probably due to a more efficient oxidation of SO_2 in air with a higher relative humidity, as was observed by Boy *et al*. (2005). Just to the opposite, the $PM_{2.5–10}$ concentration decreased with an increasing relative humidity. The explanation for this phenomenon is not quite clear, but it is most probable that when relative humidity increases, the ground also gets wet and the resuspension of coarse particles is hindered. When the relative humidity is low, the streets are expected to get dry. A higher proportion of $PM_{2.5–10}$ during the dry season was observed also in the study by Harrison *et al*. (2001). The concentration of NO_x showed a slight decrease with an increasing relative humidity.

Mixing height

Similar analysis did not reveal any clear correlation between the pollutant concentrations and the mixing height. However, when analysing the diurnal variations of the local traffic-related pollutants of BC and NO_x (Appendix Fig. A10) in different seasons, there were clear, elevated concentrations seen during situations when the daily-averaged mixing height was at its lowest (less than 240 m). With higher mixing heights (above ~200 m), their concentrations were quite similar to one another. Most clearly, the increased BC and NO_x concentrations during the low mixing height situations were seen during

the autumn and winter when the diurnal variation of the mixing height was at its lowest (Appendix Fig. A6).

In some studies (e.g., Wagner *et al*. 2017, Kurppa *et al*. 2018), it was shown that an increasing mixing height can effectively dilute local pollutants. However, it was also shown that especially inside street canyons, correlations between the mixing height and pollutant concentrations are poor (Schäfer *et al*. 2006). Earlier studies in the Helsinki area showed that for the studied parameters (traffic, wind speed and mixing height), the mixing height was always the less explanatory one (Järvi *et al*. 2008). The study of Järvi *et al*. (2008) was made at a site that had less characteristics of a street canyon.

Regression analysis

A simple multiple linear regression model was used to analyse the relationship between meteorological conditions and measured pollutant concentrations in the Helsinki city centre. The aim of this analysis was also to see if the regression analysis gives similar results as the methods used in the preceding sections. The Pearson correlation coefficient (r^2) was used to describe the correlation. The studied local pollutants were BC, NO_x, organics and $PM_{2.5–10}$, since the dependencies between these pollutants and meteorological parameters were found (see discussion above). The chosen meteorological parameters were wind speed, wind direction, temperature, relative humidity and mixing height. The meteorological parameter that gave the highest correlation coefficient (r^2) with the pollutant was used as an independent variable in all the models and the other meteorological parameters were added one at a time as the second independent variable. Prior to the analysis, a logarithmic transformation was made for the pollutants and meteorological parameters (log10) in order to ensure that the data is normally distributed.

The highest correlations between the selected pollutants and meteorological parameters were between BC or NO_x and wind speed (r^2 = –0.31 and –0.38, respectively), between $PM_{2.5–10}$ and relative humidity (r^2 = –0.45), and between organics and temperature (r^2 = 0.43). For BC, the best results were obtained when the wind speed together with wind direction were used in the multilinear model (smallest residual standard error, highest *t*-test, *F*-test and adjusted *R*-squared) values. For NO_x using the wind direction as the second parameter in the model also gave the best results, but nearly as good results were obtained when using the relative humidity as a second parameter. For $PM_{2.5–10}$, the best results were obtained when the relative humidity and wind speed were used as independent variables. For organics, the best results were obtained with a model that used the temperature and wind speed as independent variables. The simple statistical analysis using Pearson correlation and multilinear regression with two independent variables gave similar dependencies between the local pollutant concentrations and meteorological parameters as found in the previous chapters.

Conclusions

The concentration of gaseous and particulate pollutants were measured in the Helsinki city centre from May 2013 to April 2015. The determined components were O_3, NO, NO_2, $PM_{2.5}$, PM_{10} and the major chemical composition of PM_1. On average, the majority of PM_1 consisted of organics (60%), followed by almost equal mass fractions of sulphate (12%), BC (11%) and nitrate (9.8%), while ammonium constituted a slightly smaller portion of PM_1 (6.5%).

Comparison of the diurnal cycles of pollutants revealed that there were three different pollutant sources in the Helsinki city centre: 1) local traffic-related emissions (motor vehicle exhaust and road dust) that were shown by the higher concentrations of BC, NO_x and coarse particles during morning rush hours; 2) long-range and regional transport of pollutants to the Helsinki city centre, increasing especially the concentrations of sulphate, nitrate and ammonium; as well as 3) local source of organic aerosol other than traffic — either primary or secondary. There was some indirect evidence that at least part of organic aerosol in summertime was secondary organic aerosol. Due to two different local PM_1 sources, the concentration of PM_1 remained high during

the entire morning. Before noon, the high PM_1 was related to the local motor vehicle emissions and in the afternoon, elevated concentrations of organics increased the PM_1 concentration.

In order to understand the role of local meteorology on pollutant concentrations in the Helsinki city centre, the relationship between pollutant concentrations and meteorological parameters was investigated. It was found that the wind speed and temperature were the two meteorological parameters that affected most the pollutant concentrations. Typically the highest pollutant concentrations were measured with the extreme values of these two meteorological parameters. It seems that high wind speeds clean and dilute air from gaseous pollutants and $PM_{2.5}$, but at the same time, increase $PM_{2.5–10}$ markedly of the surrounding air if street surfaces are dry and dusty. $PM_{2.5}$ and particulate organic matter showed higher concentrations during higher temperatures, which may be at least partly due to locally-produced SOA; while during low temperatures, $PM_{2.5}$ was elevated because of local pollutants trapped in the boundary layer (inversion). It seems that with moderate wind speeds and temperatures, the air quality stays in good level in the Helsinki city centre if the role of road dust is excluded. The worst air quality, on the other hand, is expected either during very cold or warm temperatures coupled with calm winds.

This study demonstrates that air quality in the city centre is a combination of the intensity and characteristics of local particle sources and meteorology. Improving air quality in urban areas is a challenging task, but more detailed knowledge on pollution sources and the factors affecting the pollutant levels is a key tool towards a cleaner environment.

Acknowledgements: This research was funded of the Cluster for Energy and Environment (CLEEN Ltd); Measurement, Monitoring and Environmental Assessment (MMEA, work package 4.5.2) and Tekes INKA-ILMA/EAKR, NAQT and Cityzer projects. Support from Uudenmaan liitto via HAQT project is gratefully acknowledged.

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Appendix

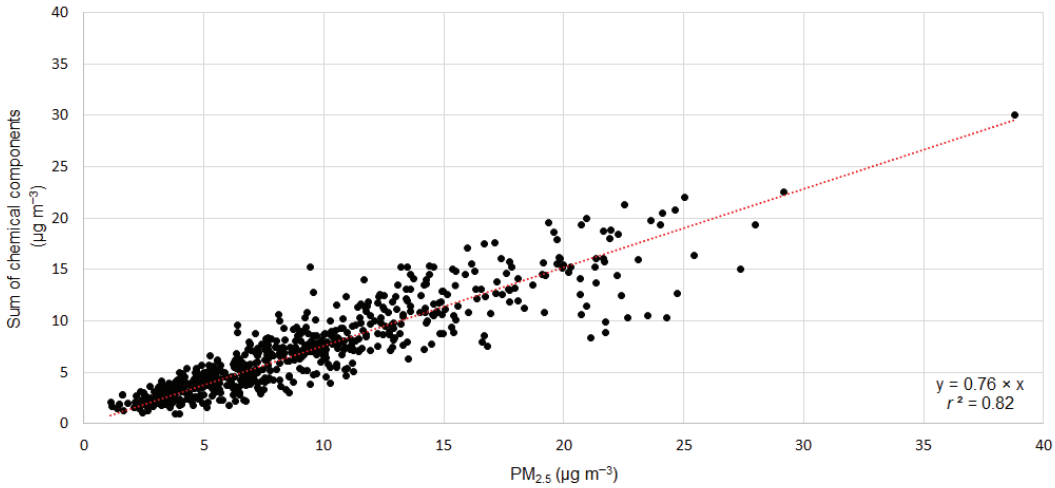

Fig. A1. Correlation between the mass concentration (calculated by summing the measured chemical components) and the measured $PM_{2.5}$ mass concentration (daily averages).

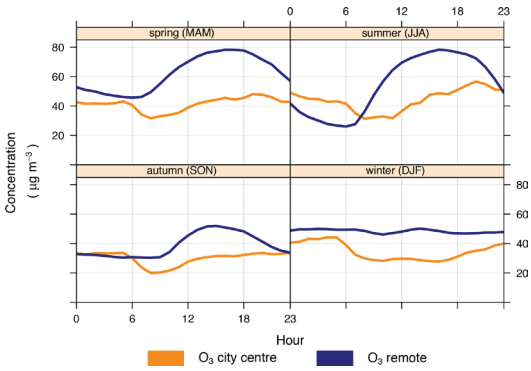

Fig. A2. Diurnal variation of O_3 in the Helsinki city centre and a remote site in the Helsinki metropolitan area during different seasons.

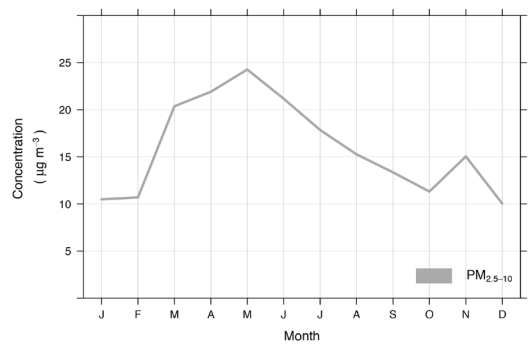

Fig. A3. Monthly mean concentrations of $PM_{2.5–10}$ in the Helsinki city centre between May 2013 and April 2015.

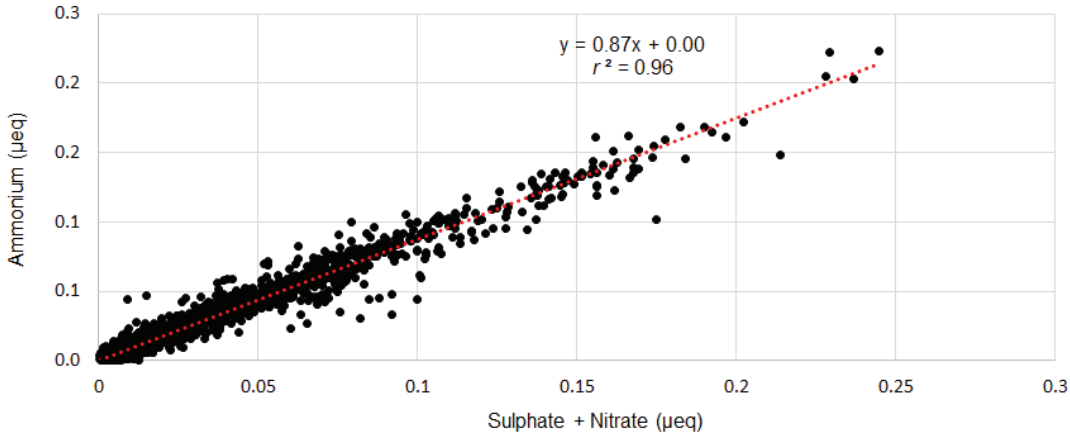

Fig. A4. Correlation between the measured ammonium concentrations and the sum of sulphate and nitrate concentrations in microequivalents.

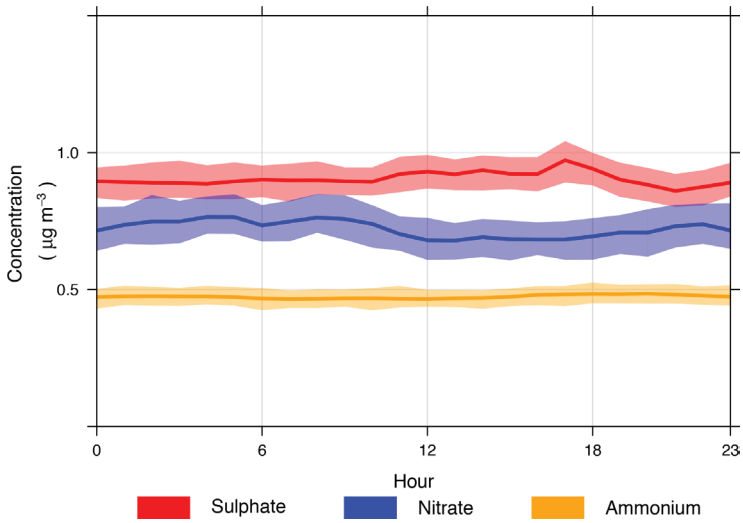

Fig. A5. Diurnal variations of sulphate, nitrate and ammonium between May 2013 and April 2015 (mean and 95% confidence interval in mean).

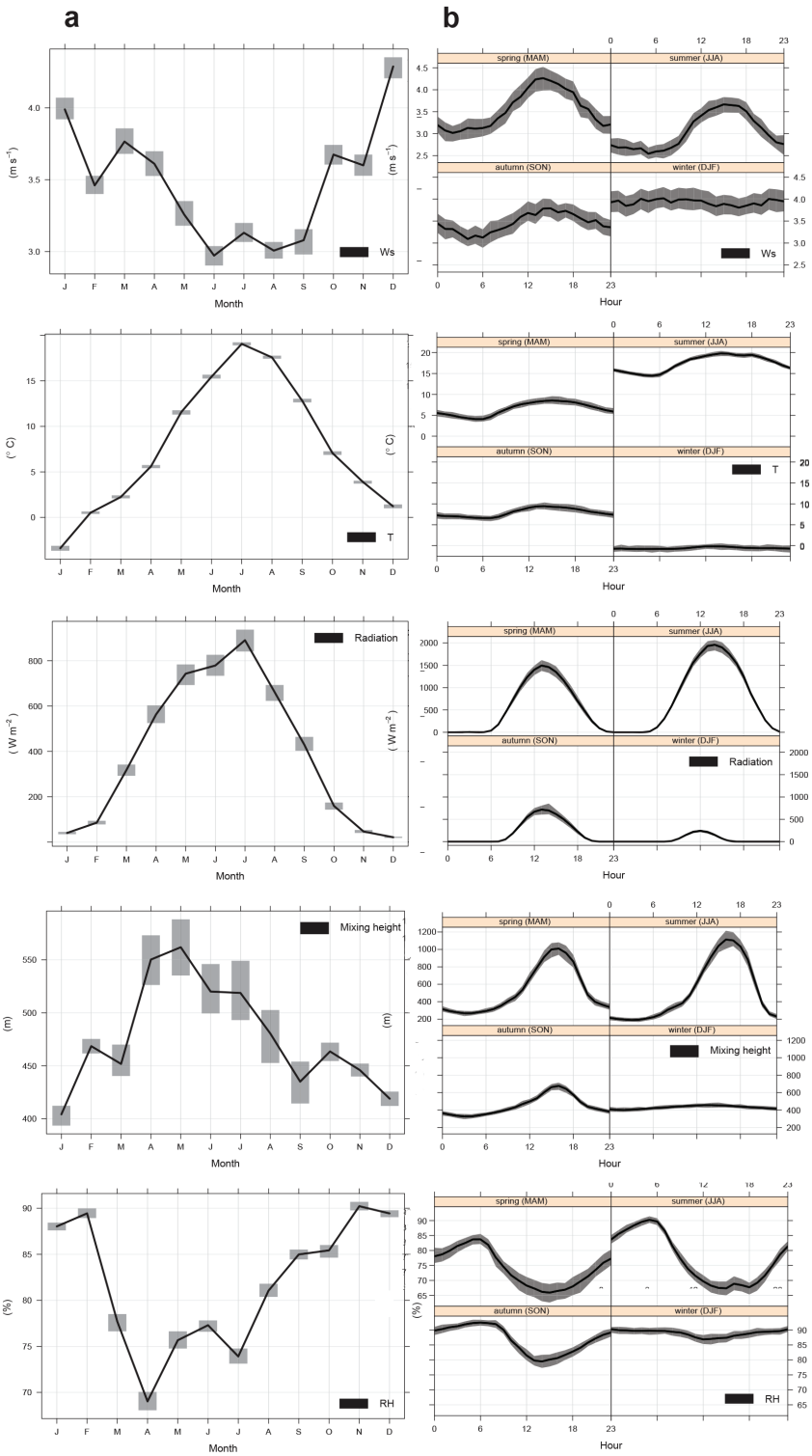

Fig. A6. (**a**) Monthly and (**b**) hourly seasonal variations of wind speed (Ws), temperature (T), radiation, mixing height and relative humidity (RH) in the Helsinki city centre between May 2013 and April 2015 (mean and 95% confidence in mean).

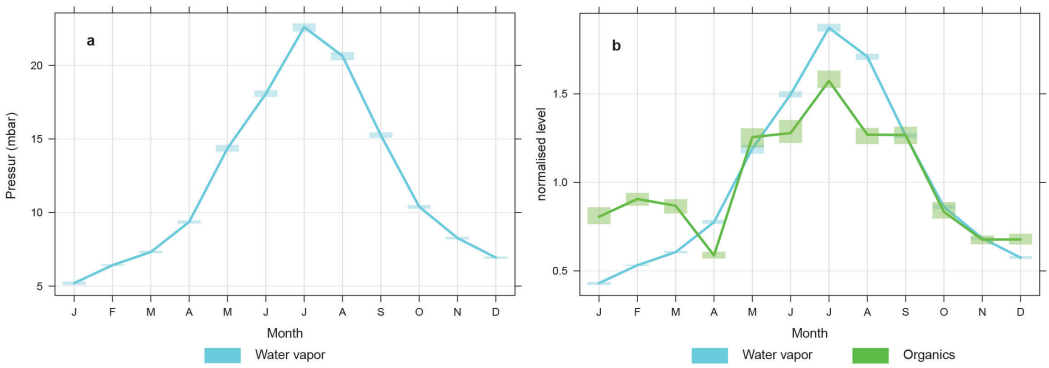

Fig. A7. Monthly-averaged (**a**) partial pressure of water vapor and (**b**) water vapor pressure and the concentration of organics (normalized y-scale) in Helsinki between May 2013 and April 2015 (mean and 95% confidence mean). Water vapor pressure is calculated from the measured meteorological parameters (relative humidity, temperature and pressure) using the formula given in Seinfeld and Pandis (1998).

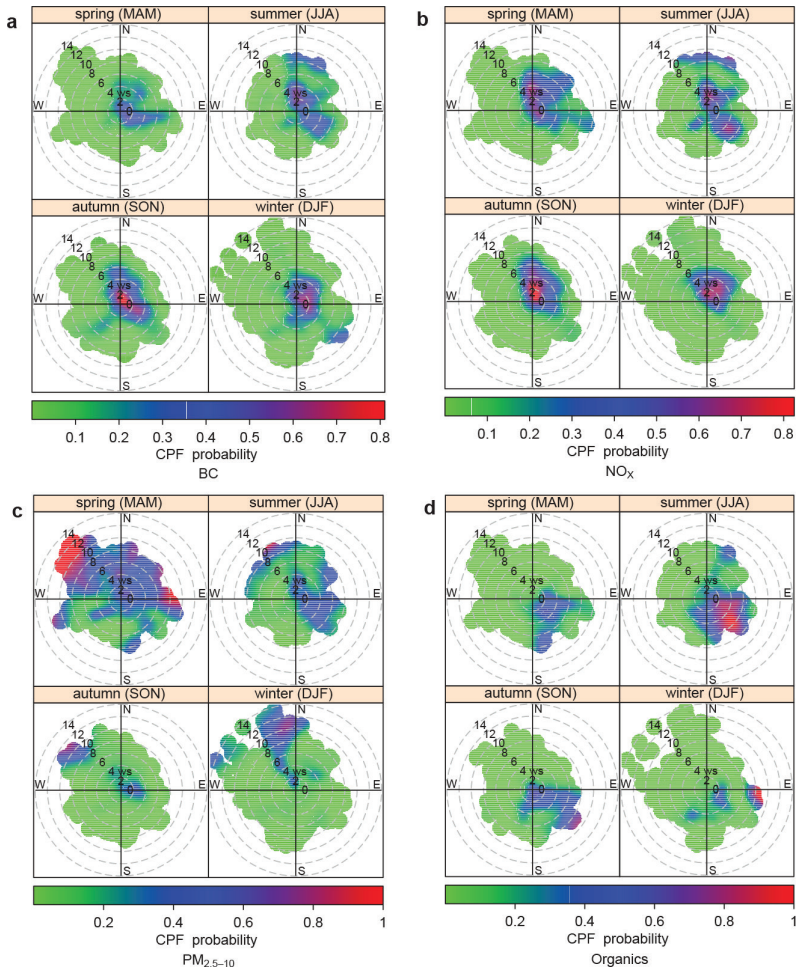

Fig. A8. Bivariate polar plots for (**a**) BC, (**b**) NO_x, (**c**) $PM_{2.5–10}$ and (**d**) organics showing the highest pollutant concentration (75th percentile) for different wind speed and direction bins.

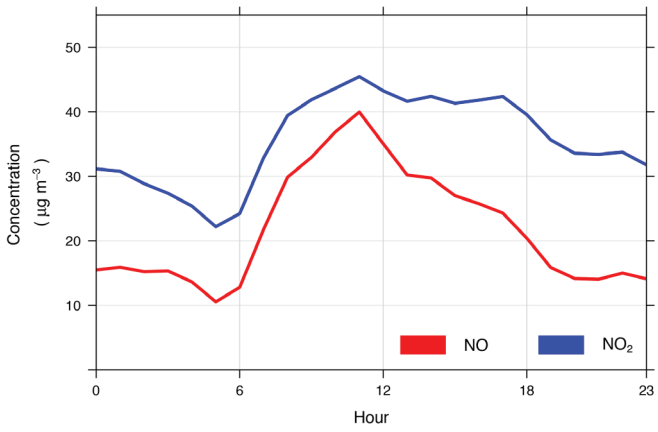

Fig. A9. Diurnal variations of NO and NO_2 during different seasons in the Helsinki city centre.

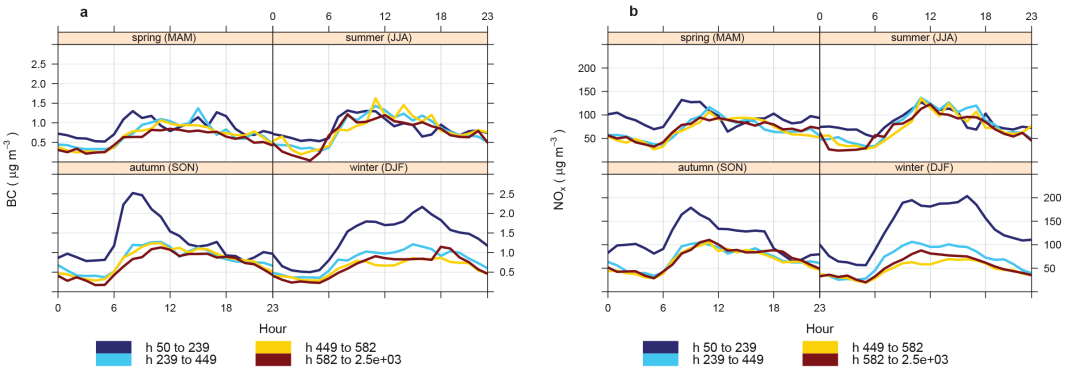

Fig. A10. Diurnal variations of (**a**) BC and (**b**) NO_x during different seasons in the Helsinki city centre. For each season, the mixing height is divided into four categories and the diurnal variation of the pollutants for each of these categories are shown.